

## PETROLEUM ASPHALTENE THERMAL REACTION PATHWAYS

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### INTRODUCTION

The industrial trend toward processing comparatively refractory heavy crudes and residua that can contain appreciable portions (10%-30%) of asphaltenes assures interest in their thermolysis. Most previous pyrolyses of asphaltenes have been oriented toward either elucidation of their structure (1,2) or the identification of fragmentation products and the dependence of their yields on pyrolysis temperature (3-6). Pyrolysis kinetics related to global product fractions (e.g. asphaltene, maltene, coke) have also been reported (2,7). Little information exists, however, about the variation of the yields of the individual constituents of the product fractions with both time and temperature. Further, operative thermolysis mechanisms, e.g. pericyclic or free-radical, are obscured in the complexities of the reactions of actual asphaltenes. The foregoing motivated the present investigation of the pyrolysis of both precipitated asphaltenes and an asphaltene model compound, pentadecylbenzene.

### EXPERIMENTAL

The asphaltenes were isolated from an off-shore California crude oil via a standard procedure of precipitation with 40 volumes of n-heptane. Pentadecylbenzene (PDB), 99.4% by GC analysis, was obtained from Alfa Products and used as received.

#### Reactors

The isothermal, batch pyrolyses were at temperatures between 350°C and 450°C for times ranging from 5 to 180 minutes. Two reactors were used. The first, used in asphaltenes' thermolyses, consisted of nominal 3/8 in stainless steel capped Swagelok port connectors attached to the two ends of a union tee. A reducer connected the center port of the tee to a 12 in length of 1/4 in o.d. stainless steel tubing. A 1/4 in Whitey severe service union bonnet valve interposed in the tubing served as a shut-off valve and also allowed attachment of a gauge for measurement of pressure. The second reactor, used in model compound pyrolyses, was assembled from a nominal 1/4 in port connector and two 1/4 in caps.

#### Procedure

For the asphaltene thermolyses the reactors were typically loaded with 1 g of asphaltene and purged with argon. The shut-off valve was then closed, and the reactor plunged into a Tecam fluidized sandbath that had been preheated to the pyrolysis temperature. After the desired reaction time had elapsed the reactor was removed from the sandbath and immediately immersed in ice water to quench the reaction. After the reactor assembly had cooled and equilibrated at room temperature, the number of moles of gas produced during pyrolysis was estimated by measuring the reactor pressure. The gaseous products were subsequently analyzed by

gas chromatography. After removing the tubing and the shut-off valve, a small amount of phenylether was added to the reactor contents to serve as an external standard in the ensuing chromatographic analysis of the heptane-soluble products. The reaction products were next subjected to a series of solvent extractions (8) to separate and collect the pyrolysis product fractions which were subsequently analyzed gravimetrically and by GC and GC-MS.

During a typical model compound experiment, reactors were loaded with about 50 mg of PDB and then 3 mg of diphenylmethane was added to serve as an internal standard in the chromatographic analysis. After purging with argon, the reactors were sealed, immersed in the preheated sandbath, and after the desired reaction time had elapsed, removed from the sandbath and quenched in cold water. Once cool, the reaction products were collected in acetone and analyzed by GC.

## RESULTS AND DISCUSSION

### Asphaltene Thermolysis

Asphaltene pyrolysis products and global kinetics are summarized in Table 1, which lists, for reactions at 350, 400 and 450 °C, respectively, holding time, product identification, product yields, and the apparent first order rate constant for asphaltene decomposition.

Pyrolyses at 350 °C yielded gas, maltene (heptane-soluble), and unreacted asphaltene (heptane-insoluble, benzene soluble) product fractions. Coke (heptane-insoluble, benzene-insoluble) did not form, and mass balance closure averaged 97%. The ultimate asphaltene conversion was less than 10%. Within the product fractions listed above, the most abundant of the individual products were the light nonhydrocarbon and hydrocarbon gases  $H_2S$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $n-C_4H_{10}$ , and  $n-C_5H_{12}$ . The maximum total gas yield observed was about 1.0% after 150 min. The maltene fraction yield was about 10% by weight of the original asphaltene after 150 min at this temperature. No individual product constituted a major portion of the maltene fraction but a series of n-paraffins was identified with each present in trace amounts.

Asphaltene thermolysis at 400 °C produced coke in addition to gas, maltene, and asphaltene fractions. Mass balance closure varied from 79% to 98%. Major gaseous products at 400 °C were  $H_2S$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $n-C_4H_{10}$ , and  $n-C_5H_{12}$  along with lesser amounts of  $CO_2$  and  $C_2H_4$ . The n-alkanes up to  $C_{26}$  and various cycloalkanes were the most abundant products in the maltene fraction at this temperature. The single-ring aromatics toluene and the xylenes were also detected in smaller proportions.

Figure 1a summarizes the temporal variation of the yields of pyrolysis product fractions at 400 °C. Maltenes were more abundant than gases at all times, and the nearly discontinuous rate of generation of coke at 30 min coincided with rapid asphaltene conversion. Note that during this period of apparently rapid asphaltene reaction the yields of gas and maltene did not increase dramatically.

Figure 1b shows the effect of reaction time on the yield of the major gaseous products.  $H_2S$  was once again the major product and its yield reached an asymptotic value of about 18 mg/g asphaltene after 120 min. This represents about 23% of the sulfur content of the original asphaltene.

Figure 1c depicts the temporal variations of selected n-paraffins at 400 °C. The yields of each alkane were nearly equal initially, but at longer times yield decreased as carbon number increased. Note that eicosane and tetracosane exhibit maximum yields. This behavior indicates that these alkanes underwent secondary decomposition.

Asphaltene pyrolysis at 450 °C produced gas, maltenes, coke, and unconverted asphaltene. Mass balances ranged from 60% to 74%. Asphaltene conversion, to predominantly coke, was rapid, and was complete after

30 min. The major constituents of the gaseous fraction were saturated hydrocarbons along with  $H_2S$ , and the identified maltenes included cyclopentane, methylcyclopentane, methylcyclohexane, toluene, cyclohexane, xylenes, naphthalene, and  $C_5$  to  $C_{26}$  n-paraffins.

For pyrolysis at  $450^\circ C$ , the proportions of the product fractions at 90 min aligned in the descending order of coke, gas, and maltene. Within the gas fraction  $H_2S$  was a major product, and its nearly constant yield of  $\approx 16$  mg/g was of the same magnitude as the yields of methane and ethane. The yields of saturated hydrocarbon gases increased steadily with time even after 30 min where asphaltene conversion was complete. Thus in addition to primary routes from the asphaltene, light hydrocarbon gases were also produced by secondary reactions of the maltenes and/or coke.

#### Pyrolysis Pathways

Petroleum asphaltene are generally considered to comprise peri-condensed aromatic units linked by aliphatic, naphthenic, or heteroatomic functionalities. The peripheries of these aromatic sheets are highly substituted by similar moieties (9-12). The present results combine with the foregoing interpretation of asphaltene structure to permit resolution of asphaltene pyrolysis pathways as well as the secondary reactions of primary products. The heteroatomic gases  $H_2S$  and  $CO_2$  were the major primary products observed from low temperature thermolyses and likely evolved from scission of low-energy thioether and carboxylic acid moieties respectively. Higher temperature primary products that arose from fragmentation of carbon-carbon bonds were hydrocarbon gases, cycloalkanes and paraffins. It would thus be consistent that the coke observed is actually the aromatic asphaltenic core stripped of its peripheral substituents. This strictly primary product evidently transforms from benzene-soluble to benzene-insoluble over a very small "window" of degradation (see Figure 1a).

The products in the maltene fraction clearly undergo secondary reactions. This is substantiated by the maximum maltene and total paraffin yields observed at 400 and  $450^\circ C$  (see Table 1) which are consistent with the notion of consecutive reactions.

Figure 2 is a summary of the reaction pathways suggested above. Primary asphaltene reactions produce asphaltenic core (coke), maltenes, and gas. Secondary reactions include fission of maltenes to lower molecular weight maltenes and gases, as well as reaction of the core to gas. Note that severe overreaction of primary products is not required to predict the formation of large quantities of benzene-insoluble solid materials. This network is similar to that proposed by Schucker and Keweshan (2) and supported by Speight and Pancirov (1).

#### Pentadecylbenzene Thermolysis

A summary of PDB pyrolyses at 375, 400, 425, and  $450^\circ C$  is given in Table 2, which lists typical data concerning holding times, major products yields, product groups (i.e. homologous series) yields, and observed first-order rate constants.

Pyrolysis of pentadecylbenzene (PDB) at  $400^\circ C$  yielded toluene, 1-tetradecene, n-tridecane, styrene, and ethylbenzene as major products. Also appearing at the longer reaction times in lower yields were a series of n-alkanes and  $\alpha$ -olefins containing 6 to 14 carbon atoms as well as 1-phenylalkanes and phenylolefins ( $\alpha$ -phenylalk- $\omega$ -enes) with alkyl chains containing 2 to 12 carbon atoms. Phenylbutene was not detected. The ultimate PDB conversion was 73% at 180 minutes. The Identified Products Index (IPI), herein defined as the total weight of all identified GC-elutable products divided by the weight of PDB initially loaded in the reactor, averaged 87%. The molar balance on aromatic rings averaged 86%. Charring occurred at this temperature.

Figure 3 illustrates the temporal variations of the yields of the major products at  $400^\circ C$ . Toluene was the most abundant product throughout the course of the reaction. The 1-tetradecene yield followed toluene

initially, but its yield decreased after reaching a maximum value at 80 minutes. The n-tridecane yield increased steadily at this temperature. During the initial 45 minutes of reaction, the styrene yield exceeded that of ethylbenzene, but after that time its yield decreased while the ethylbenzene yield continued to increase.

PDB thermolysis at 425 °C resulted in products identical to those observed at the lower temperatures. The ultimate PDB conversion was 98% after 180 minutes. The IPI averaged 70% but ranged from 98% at short times to 43% at 180 minutes. Char was observed in the reactor, so this product, along with a few unidentified products, may account for the balance of the material. The aromatic ring molar balance averaged 88%.

Table 2 shows that toluene was once more the major product. For short times of less than 15 minutes, 1-tetradecene followed toluene in abundance. The other major products aligned in the order n-tridecane, styrene, and ethylbenzene. As the reaction progressed however, the tetradecene and styrene yields decreased rapidly, and the n-tridecane yield decreased less rapidly. At 150 minutes the product alignment was toluene (50.4%), ethylbenzene (17.1%), tridecane (5.0%), styrene (0.4%), and tetradecene (0.4%).

#### PDB Thermolysis Pathway

A previous pyrolysis of PDB at 450 °C and 600kPa by Mushrush and Hazlett (13) revealed that the major products were toluene, styrene, n-tridecane, 1-tetradecene, and ethylbenzene. They reported no kinetic constants but did explain the observed product distribution on the basis of two-step Fabuss-Smith-Satterfield theory.

The present results, in agreement with Mushrush and Hazlett, show that the major products from PDB thermolysis at low conversion were toluene, 1-tetradecene, n-tridecane, styrene, and ethylbenzene. At higher conversions, a complete series of n-alkanes,  $\alpha$ -olefins, phenylalkanes, and phenylolefins were produced. Based on the criterion of a positive initial slope on the molar yield vs. time curve, toluene, 1-tetradecene, styrene, and n-tridecane were all primary products. Ethylbenzene was also a primary product but was produced mainly via secondary reactions. Figure 4, which shows the selectivity of PDB to each of the major products, confirms the above assignments and also suggests that toluene and 1-tetradecene were produced through the same reaction pathway since their selectivities at zero conversion were similar. Due to the rapid secondary reactions of styrene it is difficult to determine its selectivity at zero conversion. However, it does appear to be nearly that of n-tridecane. Thus styrene and n-tridecane are likely products of the same reaction path.

These experimental observations are summarized in the thermolysis pathway of Figure 5.

#### Kinetic Analysis

The overall order of the reaction of PDB was determined through a series of pyrolyses at 400 °C wherein the initial reactant concentration ranged from 0.0044M to 2.27M. Overall "first order" rate constants corresponding to the initial concentrations studied are presented in Table 2. The concentration dependence of these rate constants indicate that PDB thermolysis was 1.07 order.

Having determined the thermolysis of PDB to be essentially first order, overall PDB decomposition Arrhenius parameters of  $E^* = 55,455$  cal/mole,  $A = 1.10 \times 10^{14}$  sec<sup>-1</sup> were determined.

#### PDB Thermolysis Mechanisms

Two possible operative PDB thermolysis mechanisms are illustrated in Figure 6 and include an intramolecular retro-ene mechanism and a free-radical chain reaction. These were both considered by Mushrush and Hazlett. The retro-ene reaction involves intramolecular hydrogen transfer to produce toluene and 1-tetradecene, whereas the free-radical reaction involves a sequence of elementary steps including initiation, hydrogen abstraction,  $\beta$ -scission, and termination.

Both mechanisms are consistent with the observed first order kinetics as well as the observation that toluene and 1-tetradecene initially formed in equal yields. However, the concerted mechanism alone fails to account for the formation of all observed products. In contrast, the free-radical formed from PDB via hydrogen abstraction at the  $\alpha$ -carbon can undergo  $\beta$ -scission to produce styrene and n-tridecane, whereas the radical formed via hydrogen abstraction at the  $\gamma$ -carbon can similarly produce toluene and 1-tetradecene. Hydrogen abstraction at other positions can account for the formation of the minor products.

Rationalization of the selectivity to toluene exceeding that to styrene requires closer scrutiny. Whereas hydrogen abstraction is likely more rapid at the  $\alpha$ -carbon (C-H bond energy  $\approx 85$  kcal/mole) (14) than the  $\gamma$ -carbon (ca. 95 kcal/mole), thus suggesting formation of styrene preferably over toluene, the subsequent  $\beta$ -scission reaction step is more rapid for the  $\gamma$ -radical (C-C bond energy  $\approx 87$  kcal/mole) than the  $\alpha$ -radical (ca. 80 kcal/mole). Clearly both of these competing effects influence the relative proportions of toluene and styrene in the products. The higher toluene selectivity observed experimentally thus indicates that the favorable energetics of the  $\beta$ -scission reaction outweigh the unfavorable  $\gamma$ -hydrogen abstraction. Note, however, that the high toluene selectivity can also be accounted for by an efficacious retro-ene mechanism occurring in parallel with a free-radical mechanism.

#### Implications to Asphaltene Reactivity

Plausible extension of these model compound results to asphaltene reactivity follows. The aromatic portions of petroleum asphaltenes, in contrast to PDB, contain more than a single ring. A hypothetical average structure based on 12 condensed aromatic rings has been proposed for Athabasca asphaltene (15). Furthermore, several of these large aromatic sheets are joined together in polymeric fashion by aliphatic, naphthenic, or heteroatomic linkages (9,10,12) to form an even larger asphaltene particle. Recall that to account for the high toluene selectivity of PDB, the proposed radical mechanism required that the alkylaromatic benzylic radical be an important intermediate and serve as a chain carrier. The analogous asphaltenic alkylaromatic radicals would be markedly larger and considerably less mobile than the benzylic radical. This diminished mobility will trap the radicals near their point of origin and thus constrain them to react with nearby atoms. Furthermore, at reaction conditions, asphaltene is considerably more viscous than PDB, thus further frustrating radical diffusion and transport. These likely diffusional limitations (size and viscosity), most significant at low asphaltene conversion, may increase the initial importance of intramolecular concerted reactions (e.g. retro-ene) and free-radical reactions with neighboring moieties in asphaltene relative to the model compound reactions.

#### CONCLUSIONS

1. Asphaltene pyrolysis includes primary reactions to its aromatic core, maltene, and gas product fractions. Components in each of these product fractions undergo secondary degradation to lighter products, gas, and presumably, char.
2. The present results indicate that the Schucker and Keweshan asphaltene structural model is a reasonable one, and that the observed yields of pyrolysis products and product fractions can be interpreted using their hypothetical average structure.
3. PDB thermolysis to toluene, styrene, n-tridecane, and 1-tetradecene as major products likely occurs by a  $\beta$ -scission-dominated set of radical steps, but may include a concerted component.

## REFERENCES

1. Speight, J.G.; Pancirov, R.J. *Am. Chem. Soc. Div. Pet. Chem. Prepr.* **1983**, *28*, 1319.
2. Schucker, R.C.; Keweshan, C.F. *Am. Chem. Soc. Div. Fuel Chem. Prepr.* **1980**, *25*, 155.
3. Cotte, E.A.; Calderon, J.L. *Am. Chem. Soc. Div. Pet. Chem. Prepr.* **1981**, *26*, 538.
4. Ritchie, R.G.S.; Roche, R.S.; Steedman, W. *Fuel* **1979**, *58*, 523.
5. Moschopedis, S.E.; Parkash, S.; Speight, J.G. *Fuel* **1978**, *57*, 431.
6. Strauss, O.P.; Jha, K.N.; Montgomery, D.S. *Fuel* **1977**, *56*, 114.
7. Schucker, R.C. *Am. Chem. Soc. Div. Pet. Chem. Prepr.* **1983**, *28*, 683.
8. Savage, P.E.; Klein, M.T.; Kukes, S.G. *Ind. Eng. Chem. Proc. Des. Dev.* accepted.
9. Speight, J.G.; Moschopedis, S.E. in "Chemistry of Asphaltenes" ; Bunger, J.W. and Li, N.C. Eds.; Am. Chem. Soc. Adv. Chem. Ser. **1981**, *195*, 1.
10. Yen, T.F. in "Chemistry of Asphaltenes" ; Bunger, J.W. and Li, N.C., Eds.; Am. Chem. Soc. Adv. Chem. Ser. **1981**, *195*, 39.
11. Yen, T.F.; Wu, W.H.; Chilingar, G.V. *Energy Sources* **1984**, *7*, 275.
12. Yen, T.F. *Energy Sources* **1974**, *1*, 447.
13. Mushrush, G.W.; Hazlett, R.N. *Ind. Eng. Chem. Fundam.* **1984**, *23*, 288.
14. "CRC Handbook of Chemistry and Physics", 59<sup>th</sup> ed.; Weast, R.C., Ed.; CRC Press: Boca Raton, FL, 1978.
15. Speight, J.G. *Fuel* **1970**, *49*, 134.

FIGURE 1: ASPHALTENE THERMOLYSIS 400°C  
TEMPORAL VARIATIONS OF PRODUCTS

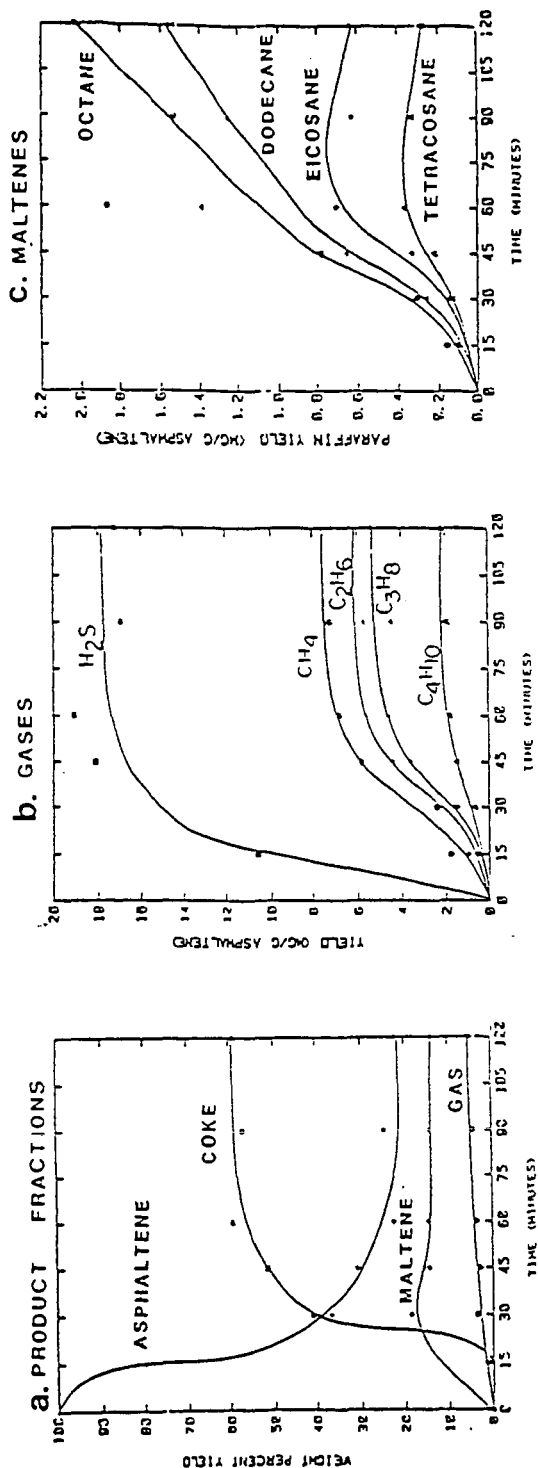


FIGURE 2: ASPHALTENE REACTION PATHWAYS

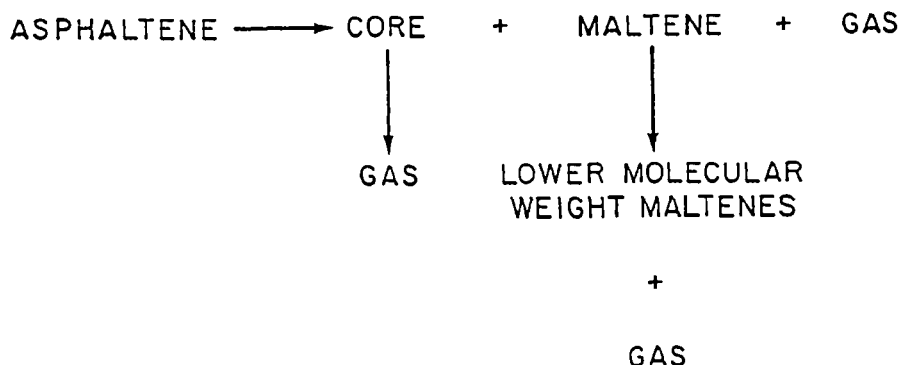


FIGURE 3  
PENTADECYLBENZENE THERMOLYSIS 400 C  
TEMPORAL VARIATIONS OF MAJOR PRODUCTS

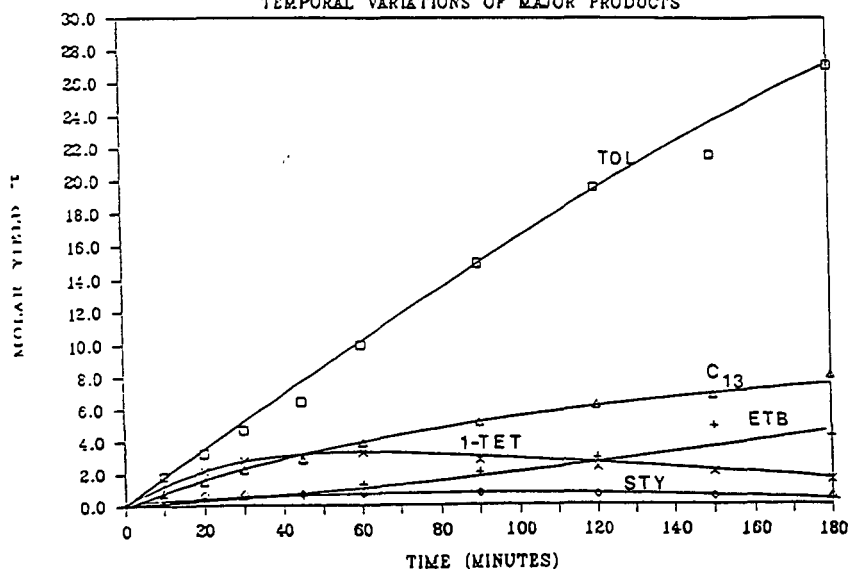




FIGURE 4: PDB SELECTIVITY TO PRODUCTS

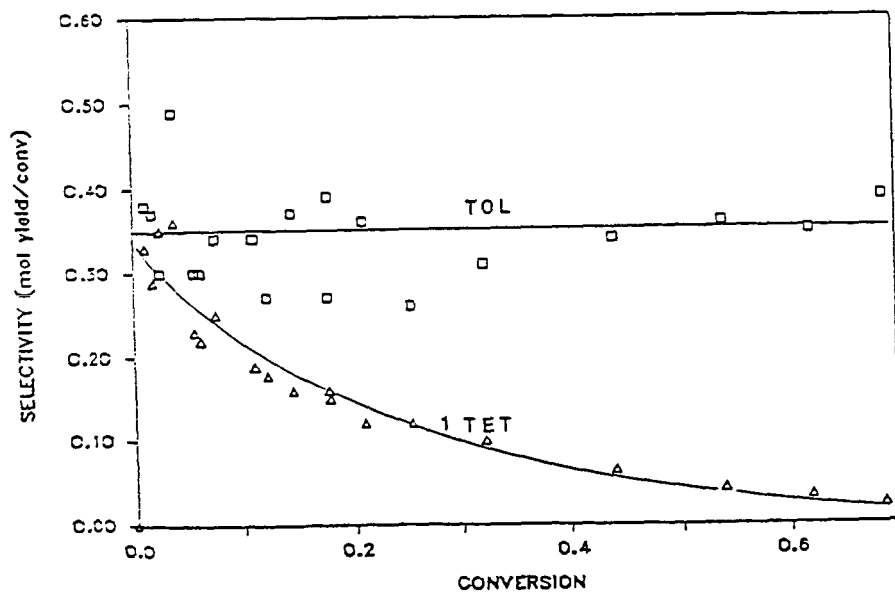
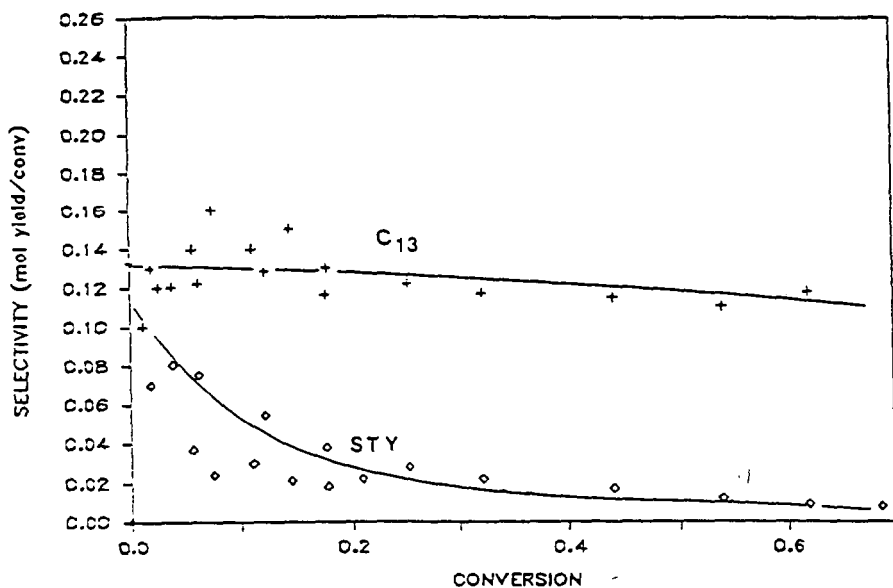


FIGURE 5  
PDB THERMOLYSIS PATHWAY

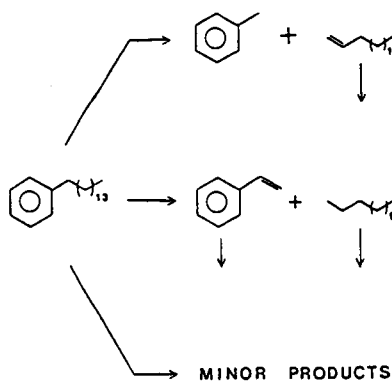


FIGURE 6 PDB THERMOLYSIS MECHANISMS

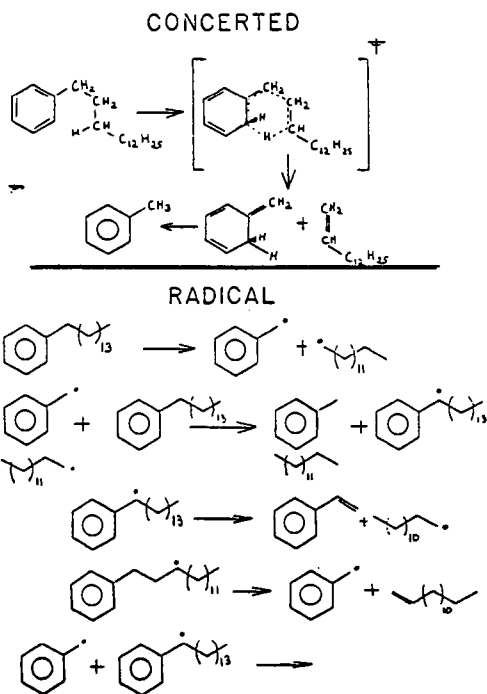


Table I  
Asphaltene Master Table

Holding Time (min)	30	60	90	30	60	90	10	60	90
Temperature	350°C			400°C			450°C		
Product Fractions (wt%)									
Asphaltene	95.9	92.6	87.0	36.6	22.6	24.6	8.7	0	0
Maltene	4.9	6.4	8.1	18.6	14.6	14.3	12.2	9.5	10.0
Gas	0.3	0.6	0.7	3.8	3.7	4.5	6.8	12.6	14.0
Coke*	0	0	0	41.0	59.1	56.6	72.3	77.9	76.0
Mass Balance	101.1	99.3	95.8	96.3	79.0	91.8	74.0	66.2	67.2
Gas Yields (mg/g)									
H <sub>2</sub> S	0.08	0.61	2.31	10.4	19.0	16.9	14.2	14.7	17.3
CO <sub>2</sub>	0.06	0.61	0.69	0.93	1.29	1.18	0.97	0.90	1.23
CH <sub>4</sub>	0.07	0.13	0.50	2.41	6.82	7.21	8.24	15.2	19.7
C <sub>2</sub> H <sub>6</sub>	-	0.05	0.26	1.63	5.59	5.70	6.52	13.2	16.8
C <sub>3</sub> H <sub>8</sub>	-	0.06	0.22	1.47	4.63	4.45	4.56	9.49	11.7
n-C <sub>4</sub> H <sub>10</sub>	-	0.03	0.09	0.64	1.77	1.92	2.12	3.50	4.24
C <sub>5</sub> H <sub>12</sub>	-	0.09	0.14	0.56	1.79	1.74	2.18	2.65	2.62
C <sub>2</sub> H <sub>4</sub>	-	0.02	0.03	0.12	0.20	0.19	0.34	0.53	0.58
n-alkane Yields (mg/g)									
n-C <sub>8</sub> H <sub>18</sub>	-	-	0.06	0.31	1.87	1.53	2.33	3.70	1.35
n-C <sub>12</sub> H <sub>26</sub>	-	-	0.05	0.26	1.39	1.25	1.83	2.12	0.95
n-C <sub>16</sub> H <sub>34</sub>	-	-	0.06	0.46	1.05	1.00	1.32	0.85	0.22
n-C <sub>20</sub> H <sub>42</sub>	-	-	0.07	0.15	0.71	0.63	0.74	0.23	0.07
n-C <sub>24</sub> H <sub>50</sub>	-	-	-	0.13	0.36	0.33	0.30	-	0.03
Total (C <sub>8</sub> -C <sub>25</sub> )	-	-	0.8	4.4	18.4	16.8	20.9	19.5	7.0
Pseudo-First Order k(min <sup>-1</sup> )	0.000597			0.01227			0.24418		

\*Coke yields are calculated by difference.

Table 2  
PDB Master Table

Holding Time (min)	30			90			150			30			90			150			10			30			60											
Temperature	375°C									400°C									425°C									450°C								
Product Yield (mol %)																																				
PDB	93.1	91.0	78.0	73.6	54.1	35.5	47.0	7.06	4.62	24.4	2.93	0.43																								
Toluene	1.88	3.84	6.98	4.68	15.0	21.6	18.1	47.4	50.4	20.9	47.9	64.5																								
1-tetradecane	1.38	2.14	2.62	2.80	2.84	2.09	3.30	0.73	0.40	3.80	0.29	0.10																								
n-tridecane	0.45	1.28	2.72	2.26	5.17	6.84	5.68	5.17	4.99	6.33	3.42	1.32																								
Styrene	0.32	0.33	0.32	0.67	0.75	0.54	1.44	0.49	0.40	2.96	0.64	0.39																								
Ethylbenzene	0.20	0.38	1.07	0.40	2.05	4.88	3.35	18.7	17.1	3.65	18.00	27.24																								
Product Group Yields (mol %)																																				
Phenyl-alkanes	3.01	5.44	15.2	7.96	24.8	37.4	31.3	79.8	81.3	35.7	77.0	101.5																								
Phenyl olefins	0.91	1.09	1.65	1.81	2.47	2.30	4.19	1.62	1.24	6.84	1.53	0.60																								
Alkanes	1.59	2.58	6.92	4.04	11.2	17.3	14.0	32.3	33.3	18.2	26.9	27.1																								
$\alpha$ -olefins	2.35	3.04	5.17	4.36	6.46	5.60	10.1	8.15	7.09	10.9	7.38	4.42																								

Pseudo-First-Order Kinetics

$C_0$ (mol/l)	$k$ (min <sup>-1</sup> )	$C_0$ (mol/l)	$k$ (min <sup>-1</sup> )	$C_0$ (mol/l)	$k$ (min <sup>-1</sup> )	$C_0$ (mol/l)	$k$ (min <sup>-1</sup> )
2.2	.00129	0.0043	.00400	2.0	.0265	1.7	0.1178
		0.0075	.00503				
		0.0150	.00535				
		0.0249	.00521				
		0.0913	.00347				
		0.482	.00452				
		1.12	.00690				
		1.80	.00783				
		2.07	.00732				
		2.29	.00690				